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TGA/FTIR study of the MCM-41-catalytic pyrolysis of tobacco and tobacco-glycerol mixtures

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Abstract

In this work, the catalytic effect of MCM-41 on the qualitative composition of the gases evolved in the pyrolysis of glycerol, tobacco and tobacco-glycerol mixtures has been studied by TGA/FTIR. The results obtained reflect that the amount of volatile products obtained from tobacco or from tobacco containing mixtures is noticeably decreased if the catalyst is used as a tobacco additive. The addition of the catalyst also produces noticeable changes in the composition of the gases obtained at each temperature. Such changes are more significant in the case of the pyrolysis of the tobacco-glycerol-mixture than in the pyrolysis of tobacco. The evolution patterns for different types of compounds reveal that the catalyst contributes to a noticeable decrease of the yields of methane, CO, CO_2 and carbonylic compounds, which could be interesting from the point of view of the use of MCM-41 as a tobacco additive in order to reduce tobacco smoke toxicity.

Keywords

TGA/FTIR, tobacco, glycerol, MCM-41, catalytic pyrolysis

Introduction

The application of the conventional techniques of thermal analysis of materials to systems involving mixtures of tobacco with different substances frequently used as cigarette additives has proved to be an interesting tool in order to obtain basic information about the different processes occurring when a cigarette is smoked [1-17]. In this way, thermogravimetry coupled with infrared spectrometry (TGA/FTIR) provides the possibility of obtaining information of the evolution of the qualitative composition of the gases evolved in such processes as the temperature increases [2-4, 13-16]. This kind of study could be interesting in order to obtain information about the cigarette smoke chemistry and toxicity that could be useful for the tobacco industry, in order to improve product design and evaluation.

The importance and need of performing studies on cigarette additives has been recognized for years by different authors [4, 18-24]. In fact, their regulation is based on their use as food or drug additives, without taking into account that such additives undergo pyrolysis and combustion processes [25, 26]. Thus, their pyrolytic behavior should be considered for establishing additional regulatory requirements for cigarette ingredients. Moreover, it should also be taken into account that the pyrolytic behavior of an isolated ingredient could be different to that presented when the pyrolysis runs are carried out with the ingredient mixed with tobacco [12]. Moreover if catalysts of the type reported elsewhere [27-29] to reduce the evolution of certain specific compounds of tobacco smoke were to be used, the interactions among the additives and the catalysts should also be taken into consideration.

Glycerol is widely used as a cigarette ingredient, acting as a moisturizing and surface active agent for flavor application. It is reported to be neither mutagenic, carcinogenic nor produce adverse reproductive effects as it is generally recognized as safe [25]. Although it seems that glycerol does not pyrolyze extensively [19, 25], the formation of acrolein and glycolaldehyde [25], as well as formaldehyde [30] as pyrolysis products has been reported.

In a previous work [13] the evolution with temperature of the qualitative composition of the gases evolved in the pyrolysis of glycerol, tobacco and tobacco-glycerol mixtures was reported, and the pathways for different groups of compounds and/or functional groups were shown. The results obtained in that work for tobacco showed that at around 100ºC, besides water evolution, some carbonyl compound generation took place, which was attributed to the decomposition of glycerol or other low molecular mass oxygenated compounds. Water, carbonyl and hydroxyl compounds and CO_2 seemed to be formed in the decomposition step associated with the glycerol loss, at around 200ºC. At higher temperatures, when the main pyrolysis step takes place, the composition of the evolved gases showed several changes depending on the temperature, and at around 240ºC water, carbonyl and hydroxyl compounds, CO_2, and $-CH_2-$ and $-CH_3$ containing compounds were evolved. As the temperature increased, CO, aromatics and methane were formed, and in the range of 410-550ºC the maxima of methyl groups, aromatics and methane appeared (please, note that the assignment of the IR band at 3016 cm^{-1} that was assigned in that work [13] to $=CH_2$ could be better assigned to methane) . At temperatures higher than 600ºC, practically only CO and CO_2 were formed. It was also observed that the presence of glycerol in the pyrolyzed mixture changed the pathway of the composition of the evolved gases, depending on the temperature, increasing the formation of water at low temperatures, $-CH_2-$ and $-CH_3$ containing compounds

at around 450ºC, CO_2 at around 340ºC, and carbonyl and carboxyl compounds at temperatures lower than 250ºC and higher than 500ºC. In that work it was reported that the glycerol condensed in the transfer line from the TG to the FTIR spectrometer, and the signal corresponding to that compound was observed during all the experiment, as a result of the entrainment of this compound by the carrier gas throughout the experiment. Barontini et al [31] have also investigated the identification and quantification of volatile species formed in the pyrolysis of tobacco by TGA/FTIR, and developed an interesting methodology based on multivariate deconvolution techniques in order to quantify the key components of interes in smoke.

Recently, a series of papers have appeared in literature on the effect of different catalysts for reducing the evolution of different compounds in the tobacco smoke. As an example, Gang Lin et al. [32] analyzed the effect of different molecular sieve materials, such as A, ZSM5 and Y type zeolites and mesoporous MCM-41 and SBA-15, on the elimination of specific tobacco nitrosamines, showing that the mesoporous materials were more effective in reducing such compounds. Vesna et al. [33] also studied the effect of the CuZSM5 zeolite on the reduction of PAHs in tobacco smoke, and Gang Lin et al. [27] studied the strong effect of ferric zeolites in reducing the specific tobacco nitrosamines in tobacco smoke. As Deng et al. pointed out [34], the use of titanate nanosheets and nanotubes permits significant reductions of harmful compounds in tobacco to be obtained. The effect of a manganese-based pigment on CO removal during tobacco pyrolysis has been also studied [35].

MCM-41 is a molecular sieve with an aluminosilicate based composition and characterized by its mesoporous structure which has been successfully tested as cigarette additive in order to reduce tobacco most smoke component yields [28]. The study of the catalytic effect of MCM-41 on the pyrolysis and oxidative pyrolysis of tobacco and mixtures of tobacco with several cigarette ingredients by Thermogravimetric analysis (TGA) has also been reported elsewhere [12, 29]. Nevertheless, no studies have been found where the effect of this type of catalysts produce on the changes suffered by the gases evolved from the pyrolysis of tobacco-catalyst and tobacco/additive-catalyst mixtures as a function of the temperature. Data on this type of systems are of paramount importance in order to know the possible interactions among the components and define future regulations and policies affecting them. In a previous work [13], we studied the thermal pyrolysis of tobacco and tobacco glycerol mixtures in the absence of catalyst. Consequently, in the present work, we focus on the qualitative study of the effect of the use of MCM-41 as catalyst on the evolution with the temperature of the composition of

the gases evolved in the catalytic pyrolysis of glycerol, tobacco and tobacco-glycerol mixtures by TGA/FTIR.

Experimental methods

3R4F cigarettes from the Reference Cigarette Program of the College of Agriculture of the University of Kentucky, glycerol (CAS number 56-81-5) with purity >99% provided by Sigma Aldrich, and MCM-41 synthesized in our laboratory have been used for the TGA/FTIR study of the pyrolysis of pure components and the mixtures thereof. The composition of the reference cigarettes as well other characteristics of this reference tobacco are reported by the supplier [36]. The proximate analysis of this tobacco provides the following results: (8.2% of moisture, 69.9% of volatiles, 10.3% of fixed carbon and 11.9% of ashes.

MCM-41 was prepared according to the procedure reported in literature [37], and characterized by the N_2 adsorption isotherm at 77 K with a Quantachrome AUTOSORB-6 with AUTOSORB DEGASSER. The BET area, the pore size distribution (according to the BJH method with cylindrical geometry of the pores and using the Harkins and Jura equation for determining the adsorbed layer thickness (*t*)) and the pore volume from the N_2 adsorption isotherms are shown in Table 1. Figure 1 shows the XRD spectra of the catalyst, obtained in a Seifert equipment, model JSO-DEBYEEFLEX 2002, showing the existence of the (100) diffraction peak and the shoulders related to the presence of aluminium [28]. The particle size of the catalyst is lower than 70 μm. The typical moisture content of catalyst at beginning of test was around 10%.

Samples of tobacco, glycerol and tobacco-glycerol mixture, with and without catalyst addition, of less than 10 mg, were pyrolyzed in an N_2 atmosphere (99.999% minimum purity) using a TGA Netzsch TG209 thermobalance at a heating rate of 35ºC/min under a nitrogen flow of 30 $mL \cdot min^{-1}$ (STP). The sample temperature was measured with a thermocouple directly attached to the crucible, i.e., very close to the sample. The heating rate was selected high enough to ensure the quality of the FTIR data obtained [38]. To ensure the measurement of the actual sample temperature, a calibration of the temperature was performed using the Curie-point transition of standard metals, as suggested by the equipment manufacturer's recommendations. The output of the gas from the TGA was connected to a Bruker Tensor 27 FTIR spectrometer through a heated line, as described in the bibliography [39]. The balance adapter, the transfer line and the FTIR gas cell were maintained at 200ºC, in order to minimize

the condensation of the less volatile compounds. On the other hand, the low volumes in the thermobalance microfurnace, transfer line and gas measurement cell permit low carrier gas flowrates to be used and allow for good detection of the gases evolved in the pyrolysis process. A lag of around 15 seconds, equivalent to 8.8ºC, has been estimated between the moment when the gases exit the TGA furnace and arrive at the IR cell. Experiments were run in duplicates and the observed differences were better than 2ºC and 2 % in weight and better than 10% in the IR signals analysed. The assignments shown in Table 2 have been considered for the interpretation of the FTIR spectra obtained at each temperature."

The reference tobacco was grinded (particle size lower than 100 μm) in order to avoid the heterogeneity associated with the different tobacco fibers, and the mixtures with glycerol were prepared by weighing the corresponding amounts of each material directly in the crucible, and carefully mixing with the aid of a fine needle. Each thermogravimetric run was repeated twice in order to test the reproducibility of results. The tobacco-glycerol mixtures were prepared by adding glycerol (around 25%, w/w) to the 3R4F grinded tobacco, directly in the TGA crucible, and mixing thoroughly with a thin needle. The total amount of glycerol is thus the sum of that added and that already contained in the reference tobacco. In order to avoid the influence of the possible changes of the homogeneity and the properties of the mixture with time, the TGA analyses were carried out immediately after each sample of mixture was prepared. The percentage of glycerol added was chosen according the results obtained in previous works [12, 13] in order to enhance the effect of the glycerol on the behavior of the mixture. For the preparation of the catalyst containing mixtures, each ingredient was weighed separately, and afterwards thoroughly mixed with the needle. As in the previous thermal studies [12], the catalyst amount was around 15% (w/w).

Results and discussion

The effect of MCM-41 on the temperature and on the relative importance of the decomposition steps in the pyrolysis of tobacco, glycerol and tobacco-glycerol mixtures has been studied by TGA and has been presented elsewhere [12]. In that work, the different decomposition steps involved in the pyrolysis of the reference tobacco were established, and an assignment to the decomposition of different tobacco fibers components was suggested. The influence of the addition of glycerol was also studied as well as the catalytic effect of MCM-41 on the relative importance and the temperature of the decomposition steps. On the other hand, the evolution with the temperature of the qualitative composition of the gases evolved from the thermal pyrolysis of glycerol, tobacco and tobacco-glycerol mixtures has also

been studied by TGA/FTIR, and the pathways followed by different types of compounds has been shown [13]. In that paper the effect of the catalyst on the evolution of the different functional groups appearing in the different compounds evolving from the TGA furnace was not considered. In the present work, we focus on the changes undergone in the chemical composition of the pyrolysis products, expressed in terms of functional groups, at each temperature when MCM-41 was added as a catalyst.

According to the previous works [12, 13], the pyrolysis of the reference tobacco involves at least 6 decomposition steps which, at 35ºC/min, take place at the following temperatures :

- evaporation of moisture at temperatures lower than 130ºC
- evaporation of glycerol and other volatile compounds in the range 160-220ºC
- two overlapped processes in the range 220-380ºC mainly corresponding to decomposition of hemicellulose and other polymers and pyrolysis of cellulose, respectively
- pyrolysis of lignin in a wide range of temperature, with maximum reaction rate at around 480ºC
- dehydrogenation and aromatization of char at around 650ºC

A first idea of the effect of the presence of catalyst can be provided by the Gram-Schmidt curves (GS curves) that, based on vector analysis, reconstruct the acquired FTIR interferograms, allowing the plots of the total evolved gases detected by the spectrometer to be obtained and thus, in an indirect way, reflecting the yield of the total volatile products obtained at each temperature. Figure 2 shows the weight loss curves (TGA curves) and the normalized GS curves obtained for the three cases studied in this work (i.e., tobacco, glycerol and tobacco-glycerol mixture) in the absence and in the presence of MCM-41. The mass percentage corresponds to the percentage of the total mass at the beginning of the experiment that remains in the crucible at each temperature. These normalized GS curves have been obtained by dividing each GS-intensity value by the mass of pyrolyzable sample weighed in each run (i.e., without considering the mass of catalyst. Thus, the pyrolyzable sample corresponds to the masses of tobacco, glycerol or tobacco+glycerol at the beginning of the experiment.). As can be seen, the normalized GS-intensities of the tobacco (Figure 2a) and tobacco-glycerol (Figure 2c) pyrolysis at temperatures higher than 150ºC are lowered by the

presence of catalyst, thus indicating a decrease of the yield of volatile products. This is a very interesting result because MCM-41 and related products are being considered as additives for reducing tobacco smoke toxicity [28]. At temperatures lower than 150ºC, the evolution of water desorbed overlaps with dehydration of glycerol, and evaporation of other volatile compounds.

The comparison of the GS curves corresponding to the pyrolysis of glycerol in the presence and in the absence of MCM-41 (Figure 2b) deserves a particular comment. As pointed out in a previous work [13], at the experimental conditions employed and in the absence of catalyst, the main loss of glycerol takes place at around 190-200ºC and is mainly due to evaporation processes. Then, the glycerol evolved condenses in the transfer line between the TGA and the FTIR equipment, and afterwards is continuously carried by the gas stream that leaves the TGA furnace, arriving at the IR cell and giving the GS curve of glycerol shown in Figure 2b. When the pyrolysis of glycerol is carried out in the presence of MCM-41, the main weight loss takes place at a temperature very close to that corresponding to the thermal process, i.e., the non-catalyzed process, as the TG-curves of Figure 2b show. However, the GS-curve indicates that the decomposition products arrive at the IR cell once the weight loss of glycerol sample in the TGA furnace has occurred. Thus, despite the noticeable differences between the GS-curves of glycerol in the presence and in the absence of catalyst, it can be concluded that the same above-mentioned process of condensation and evaporation in the transfer line might be taking place. Nevertheless, from the shape of the GS-curve corresponding to the pyrolysis of glycerol+MCM-41 it could be deduced, as will be demonstrated in the IR spectra analysis performed in the following paragraphs, that in this case, other compounds besides glycerol are being formed, that once they are condensed on the transfer line, they are being selectively desorbed as the process proceeds. Thus, the peaks and shoulders observed in Figure 2b on the GS curve of the catalytic pyrolysis of glycerol should correspond with the arrival at the IR cell of the different compounds that are successively desorbed from the transfer line. These differences between the GS curves corresponding to the thermal and catalytic pyrolysis of glycerol point out that in the presence of catalyst other processes different to evaporation could be taking place, despite due to these desorption processes, the results obtained should be interpret very carefully.

The chemical processes whose maximum reaction rate occurs at the maxima and shoulders appearing in the GS-curves of Figure 2 can be identified by the events of the corresponding volatile products generation. In this way, TGA/FTIR allows us to obtain an idea of what kind of

functional groups and chemical compounds are formed in each step, if the variation with temperature of the intensity of the FTIR bands corresponding to selected compounds or groups is followed [13]. Thus, the assignments shown in Table 2 have been considered as representative of water, aromatics, methane, $-CH_3$ and $-CH_2-$ groups, CO_2 and CO, carbonylic compounds, and C-O bonds, and their evolution with temperature for glycerol, tobacco, and tobacco-glycerol is shown in Figures 3 and 4, respectively. In order to facilitate the comparison among those systems, the absorbance values obtained in each case have been divided by the mass of pyrolyzable sample in each run (i.e., without considering the mass of catalyst). As previously commented on, in a previous work [13] we assigned the FTIR band at around 3016 cm^{-1} to C-H stretching vibrations bonds in alkenes. However, this band could also correspond to methane, if an intense band at around 1306 cm^{-1} also appears [13], as occurs in this case; therefore, the bands at 3016 and 1304 cm^{-1} have now been assigned to CH_4. As previously pointed out, the experiments carried out allow us to compare the effect of the catalyst on the tobacco, on the glycerol as well as on the tobacco-glycerol mixtures. The results shown in Figures 3 and 4reveal different behavior depending on the family of compounds considered. The differences in the temperature and in the relative importance of the several decomposition steps have been shown elsewhere [12], as well as the influence of the addition of glycerol in the FTIR results [13]. Therefore, in this work, we focus on the effect of the addition of MCM-41. The results shown in Figure 4 are in good agreement with that reported by Barontini et al. [31] for the content of CO_2, CO, water and acetaldehyde in the evolved gas from the pyrolysis of shredded tobacco.

Figure 3 shows the evolution with temperature of the FTIR selected bands appearing in the spectra of the gases evolved from the thermal and catalytic pyrolysis of glycerol. The graphics corresponding to aromatics, methane and carbon monoxide are not shown because IR bands attributed to these compounds have not been observed. The shape of the curves agrees with the corresponding GS curves, that reflects that, unlike thermal pyrolysis where there is a continuous increase of the GS intensity, practically without any marked peak, in the catalytic pyrolysis, several events of arrival of products at the IR cell take place. As previously commented on, according to the TGA and GS curves shown in Figure 2b, in the experimental conditions used in this work, the products obtained from the evaporation+pyrolysis of glycerol condense in the TGA-FTIR transfer line and are continuously desorbed as the process continues. Thus, in fact, the curves shown in Figure 3 are the result of these generation-condensation-desorption processes for the different compounds evolved. However, the study of these curves allows us to interpret and compare the pathways followed by the gases

evolved in the thermal and catalytic pyrolysis of the tobacco-glycerol mixture. The interpretation of the curves of Figure 3 requires the analysis of the FTIR spectra of the gases evolved from the catalytic pyrolysis of glycerol at selected temperatures (i.e., temperatures corresponding to the GS maxima of Figure 2a), that are shown in Figure 5. The spectra corresponding to the thermal pyrolysis of glycerol were shown elsewhere [13] and mainly appeared the water IR bands, being much less intense the glycerol bands, and also reflecting the appearance of small CO_2 bands, at around 2361 cm^{-1}, at temperatures higher than 500ºC. However, in the presence of MCM-41, the bands of glycerol at around 2882-2940 (corresponding to C-H bonds) and 1046 cm^{-1} (corresponding to C-O bonds) are much more intense than in the absence of catalyst, as well as the CO_2 band, that at temperatures higher than 500ºC becomes the most intense band of the spectrum, as opposed to the behavior observed in the absence of a catalyst, where these bands had relatively low intensity. This behavior could reflect the formation of other compounds different to glycerol that condense in the heated TGA-FTIR transfer line and could decompose yielding CO_2 at the temperature of the transfer line as the process proceeds. According to Figure 3a, water continuously arrives at the FTIR analyzer, in higher amounts in the presence of catalyst, and showing a maximum under 150ºC, related with evaporation of moisture. The presence of bands associated with carbonyl groups (1749 cm^{-1}) cannot be clearly assessed from the spectra of Figure 5, because it is overlapped with bands of water. However, the comparison of the evolution curves of water (Figures 3a) and carbonyls (Figure 3b) reveals different pathways and suggests that, even though the first maximum at around 95ºC could correspond to the overlapping with the spectrum of water, the increase of carbonylic compounds in the range of 197 and 453ºC in the presence of MCM-41 should be the consequence of the generation of compounds different than water and glycerol, probably as a consequence of some catalytic degradation of glycerol. Figure 3c shows the evolution of CO_2 and in good agreement with the spectra of Figure 5, indicates an increase of the CO_2 evolved as the temperature increases as well as the higher amount of CO_2 evolved in the presence of MCM-41. The bands selected as representative of methylene and methyl groups and C-O bonds are overlapped with the C-H and C-O bands of glycerol. Thus, the curves shown in Figures 3d, 3e and 3f could be the result of arrival at the IR cell of glycerol as well as other compounds also having the same type of chemical bonds. In fact, the differences in the temperature and the relative intensity of the maxima in Figure 3e, corresponding to methylene groups (with the main maximum at around 364ºC and the following one at 284ºC) and Figures 3d and 3f (with the main maximum at 253ºC and the following one at 364ºC) suggest that, effectively, different compounds, besides glycerol, have

been generated. These compounds are evolved in higher amounts in the presence of MCM-41.

Figure 4 shows the evolution with temperature of the different compounds evolved from the thermal and catalytic pyrolysis of tobacco and tobacco-glycerol mixtures. The differences in the temperature and in the relative importance of the several decomposition steps have been shown elsewhere [12], as well as the influence of the addition of glycerol in the FTIR results [13]. Therefore, in this work, we focus on the effect of the addition of MCM-41.

Figure 4a shows the evolution of the intensity of the band associated to water. It can be observed that the presence of the catalyst mixed with tobacco significantly reduces the amount of water evolved in the range of temperature corresponding to the main weight loss (250-400ºC). At low temperatures (lower than 150ºC), the presence of the catalyst seems to increase the generation of water in the case of the mixture, probably reflecting the evaporation and desorption of moisture from the catalyst, but to decrease the generation of water from tobacco. At temperatures higher than 450ºC the only sample producing noticeable amounts of water is the tobacco-glycerol mixture.

As can be seen, aromatics (Figure 4b) and methane (Figure 4c) follow very similar pathways for the four systems studied including tobacco, and the evolution curves are very similar, with the main difference appearing in the respective intensity values, thus suggesting that both appear as a result of the same mechanism. The yields of aromatics and methane from the tobacco are higher than from the tobacco-glycerol mixture, and reflect the dilution effect of this additive [13]. According to Figure 4, aromatics and CH_4 are mainly formed at high temperatures, with maxima in the range of 450-550ºC, and the global effect of the addition of MCM-41 results in a decrease of the yield of these compounds in both systems with and without added glycerol. Nevertheless, the catalyst could cause some increase of aromatics in the range of 250ºC and 415ºC in the case of the tobacco-glycerol mixture pyrolysis.

R-C=O (Figure 4d), CO_2 (Figure 4e), $-CH_2-$ (Figure 4f), and CO (Figure 4g) show similar trends when tobacco is present, even though some differences exist. These groups show a maximum in the range 315-340ºC and a shoulder or a peak at around 240-290ºC, depending on the system or the band. Once again, the presence of the catalyst produces large reductions in the evolution of these compounds, showing the interesting effect of this type of material on the tobacco pyrolysis behavior, in accordance with the observed reducing effect when smoking

this type of mixture [28]. Moreover, a wide step with a diffuse peak at around 460-490ºC can also be observed. The cases of carbonylic compounds and CO_2 are shown in Figures 4d and 4e, respectively, and reflect that the presence of MCM-41 decreases the yields of these compounds, but the shape of the curves, i.e., the relative importance of the peaks, is not noticeably modified, and only a slight displacement towards lower temperatures seems to take place as a consequence of the addition of the catalyst. The comparison among the curves shown in Figures 4d and 4b allows interesting results, because despite the increase of carbonylic bands in the products evolved from the catalytic decomposition of glycerol (Figure 3b), the presence of the catalyst decreases the yield of carbonyls from the tobacco-glycerol mixture. The peak appearing at temperatures lower than 150ºC in Figure 4d may be the result of an overlapping with characteristic bands at around 1800-1600 cm^{-1} of the water spectrum. The curves of CO_2 (Figure 4e) show a peak at around 640-670ºC that may correspond to the decomposition of endogenous inorganic carbonates [12].

The case of methylene groups (Figure 4f) is quite different: whereas the behavior of the thermal and catalytic pyrolysis of tobacco is relatively similar to that above-commented on of carbonylic compounds, and the catalyst reduces the yields of $-CH_2-$ groups without noticeable changes in the shape of the curves and reflecting only a small decrease of the temperatures of the maxima, the effect of the catalyst on the tobacco-glycerol mixture changes noticeably. In fact, the presence of the catalyst seems to cause an increase in the appearance of the methylene groups at temperatures lower than 290ºC and higher than 370ºC. As shown in Figure 3d, this effect cannot be attributed to the effect of MCM-41 on the added glycerol, thus suggesting the existence of some type of interaction among the components of the mixture that changes the mechanisms of reaction and the type and relative amounts of the products evolved.

The case of carbon monoxide is especially interesting because CO is one of the toxic components of the tobacco smoke that is regulated by governments. According to Figure 4g, the formation of CO starts at around 250ºC, and it is noticeably decreased in the presence of MCM-41. As in some of the previous cases, the shape of the curves does not change significantly in the presence of the catalyst and, besides the decrease of absorbance, only slight temperature displacement seems to appear. Different than the other groups, CO exhibits a marked increase of absorbance at the highest temperatures which is associated with the slow decomposition of char or coke resulting from the previous decomposition steps. Additionally, the presence of a catalyst in the pyrolysis of tobacco-glycerol mixtures produces a

separated peak at around 270ºC where a slight shoulder was observed in the absence of the catalyst.

The cases of -CH_3 (Figure 4h), on one hand, and the ether and alcohol bands at 1191 (Figure 3i) and 1047 (Figure 3j) cm^{-1}, on the other hand, are very interesting. The behavior observed for the pyrolysis of tobacco, in the presence and in the absence of catalyst is the same as that previously commented on for aromatics and methane. The corresponding curves showing the evolution with temperature in the thermal and catalytic pyrolysis of tobacco follow similar trajectories. The main difference is the lower intensity, i.e., the lower yields, obtained in the presence of MCM-41. Nevertheless, the case of the mixture is quite different and enhances the importance of and interest in performing this type of study. As seen in Figure 4h, it seems that the effect of MCM-41 results in a decrease of the yields of -CH_3 groups for samples with no glycerol, but when glycerol is present an increase is observed at all temperatures and a noticeable increase in the range of 150-360ºC, especially at around 240ºC, where a marked maximum appears. Obviously, the particular behavior of these functional groups in the catalytic pyrolysis of the mixture could be attributed to the effect of MCM-41 on the decomposition of glycerol, as the results shown in Figures 3e and 4f corroborate.

According to the previous statements, and in good agreement with the results previously reported [28], in a general way, the effect of the use of MCM-41 as a catalyst in the pyrolysis of tobacco and tobacco+glycerol mixtures is to cause a global decrease in the yields of the evolved volatile compounds. This effect can be clearly pointed out if the areas under the curves on Figure 4 are evaluated. Although the results obtained do not actually represent a measurement of the yields or amounts of each type of functional group, there is a proportionality, and the comparison of the areas obtained for each system could be considered as an indirect measurement of the influence of the catalyst. Thus, Table 3 shows the values of the areas obtained for each family of compounds and for each system. As can be seen, the reductions provided by MCM-41 are clear in all the cases, with the only exception of the already mentioned cases of -CH_3, -CH_2- and the C-O groups in the tobacco+glycerol mixture, that as Figure 3 reflects is related with the pyrolytic behavior of glycerol+MCM-41 under the experimental conditions used in this work. These results enhance the need to perform studies focused on the particular pathways followed by the ingredients used in the fabrication of commercial cigarettes and their interaction with the different materials that may be used as additives for toxicity reduction.

Conclusions

The results obtained in this work show the catalytic effect of MCM-41 on the pyrolysis of tobacco and tobacco-glycerol mixtures, and the changes in the qualitative composition of the gases evolved at each temperature, when the pyrolysis process is carried out under dynamic conditions, at 35ºC/min. Thus, the total amount of gases evolved is noticeably decreased by the addition of the catalyst and, moreover, significant changes in the instantaneous proportions of the different compounds appearing in such gases is also observed. The yields obtained at each temperature for the different functional groups studied show an interesting decrease of the amounts of CO_2, CO, CH_4 and carbonylic compounds as a consequence of the addition of MCM-41. On the other hand, MCM-41 also has a noticeable effect on the pyrolytic behavior of glycerol, and may cause the higher extent of the pyrolysis of glycerol in relation to the evaporation processes, with the formation of other products different than glycerol or water.

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Figure captions

Figure 1. XRD spectrum of the synthesized MCM-41

Figure 2. TGA and normalized GS curves corresponding to the pyrolysis of tobacco (a), glycerol (b) and tobacco+glycerol (c) in the absence and in the presence of MCM-41. The GS normalized curves have been obtained by dividing the GS intensity by the mass of pyrolyzable material.

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Figure 5. FTIR spectra of the gases evolved from the thermal and catalytic pyrolysis of glycerol at selected temperatures. The scale has been displaced in order to facilitate the spectra comparison

Table captions

Table 1. Textural properties of MCM-41 from the N_2 adsorption isotherms at 77K

Table 2. IR bands selected for the analysis of the evolution with temperature of the pyrolysis gases [13, 34, 35].

Table 3. Measured areas under the curves of Figure 2.

Table 1. Textural properties of MCM-41 from the N_2 adsorption isotherms at 77K

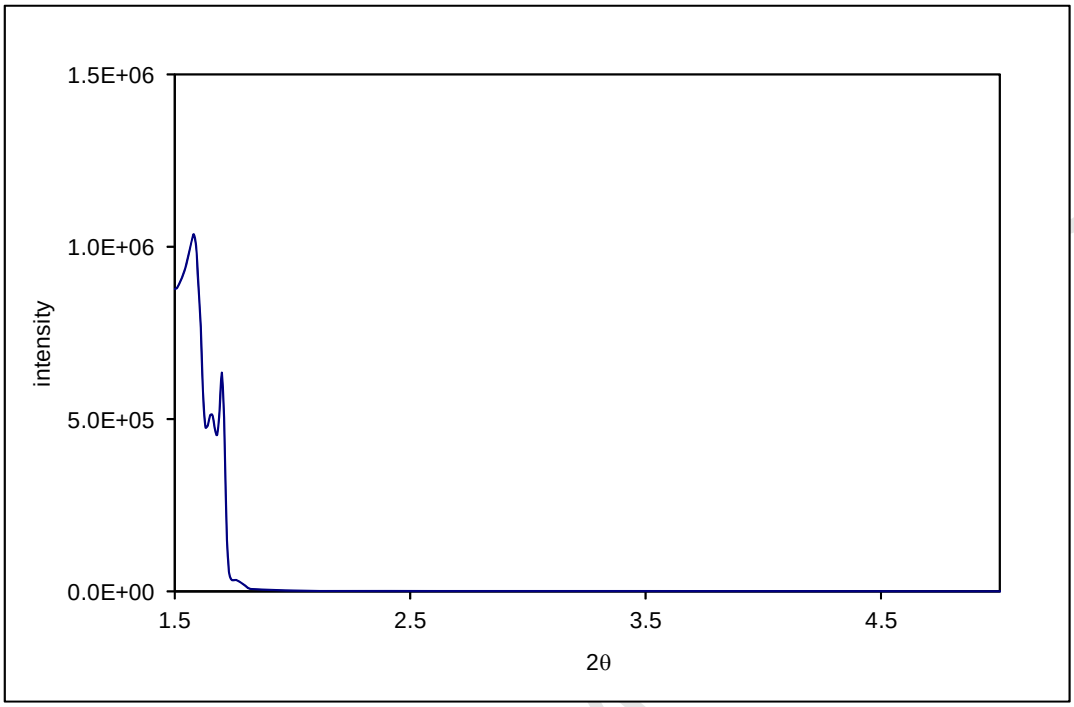
Property	**MCM-41**
Pore Size (nm) (BJH method)	2.4
BET Area (m^2/g)	874.1
Pore Volume (cm^3/g) (measured at P/P_0=0.995)	0.697

Table 2. IR bands selected for the analysis of the evolution with temperature of the pyrolysis gases [13, 34, 35].

Wavenumber (cm^{-1})	origin	Assignment
3640-3550 (selected: 3566)	O-H Symmetrical and asymmetrical stretching	Water
3130-3070 1600-1500 900-670 (several) (selected: 3076)	Aromatic C-H in plane bend Aromatic C=C-C ring stretch Aromatic C-H out of plane bend	Aromatics and heterocycles with 2 C=C as furan and furfural
3040-3010 1600-1680	C-H stretch in alkenes (in $=CH_2$) C=C stretch	Alkenes
3016 (selected) 1304	C-H stretch in CH_4 C-H symmetrical bending in CH_4	Methane
2970-2950 2880-2860 1470-1430 1380-1370 2935-2915 2865-2845 1485-1445 (selected: 2968, 2835)	Methyl C-H asymmetric stretch Methyl C-H symmetric stretch Methyl C-H asymmetric bend Methyl C-H asymmetric bend Methylene C-H asymmetric stretch Methylene C-H symmetric stretch Methylene C-H bend	Alkanes or alkyl substituents
2400-2224 (selected: 2361)	Asymmetrical stretching in O=C=O	CO_2
2180-2108 (selected: 2195)	Stretching vibration in CO	CO
2250		HNCO
1900-1600 (selected: 1749)	Carbonyl groups	Aldehydes, ketones
1050-1200 (selected: 1047, 1191)	C-O stretch	Alcohols, phenols, ethers
3400-3325 1130-1360	N-H stretch C-N stretch	
966		NH_3
714		HCN

Table 3. Measured areas under the curves of Figure 2

	Tobacco	Tobacco + MCM-41	Tobacco + glycerol	Tobacco + glycerol + MCM-41
H2O	0.155	0.109	0.203	0.155
Aromatics	0.045	0.032	0.056	0.053
CH_4	0.188	0.123	0.172	0.118
$-CH_3$	0.188	0.113	0.165	0.188
$-CH_2-$	0.066	0.041	0.058	0.079
CO_2	1.607	1.091	1.243	0.723
CO	0.075	0.041	0.065	0.024
C=O	0.314	0.216	0.303	0.250
C-O (1191 cm^{-1})	0.170	0.110	0.118	0.148
C-O (1047 cm^{-1})	0.161	0.094	0.099	0.328



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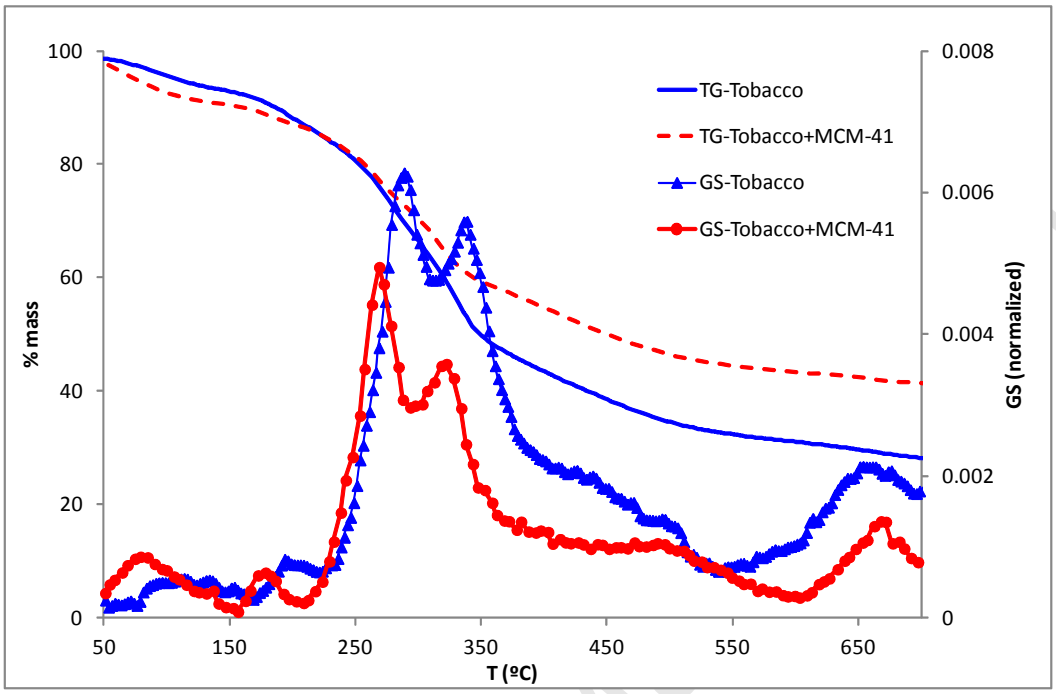

Figure 2a)

Figure 2. TGA and normalized GS curves corresponding to the pyrolysis of tobacco (a), glycerol (b) and tobacco+glycerol (c) in the absence and in the presence of MCM-41. The GS normalized curves have been obtained by dividing the GS intensity by the mass of pyrolyzable material.

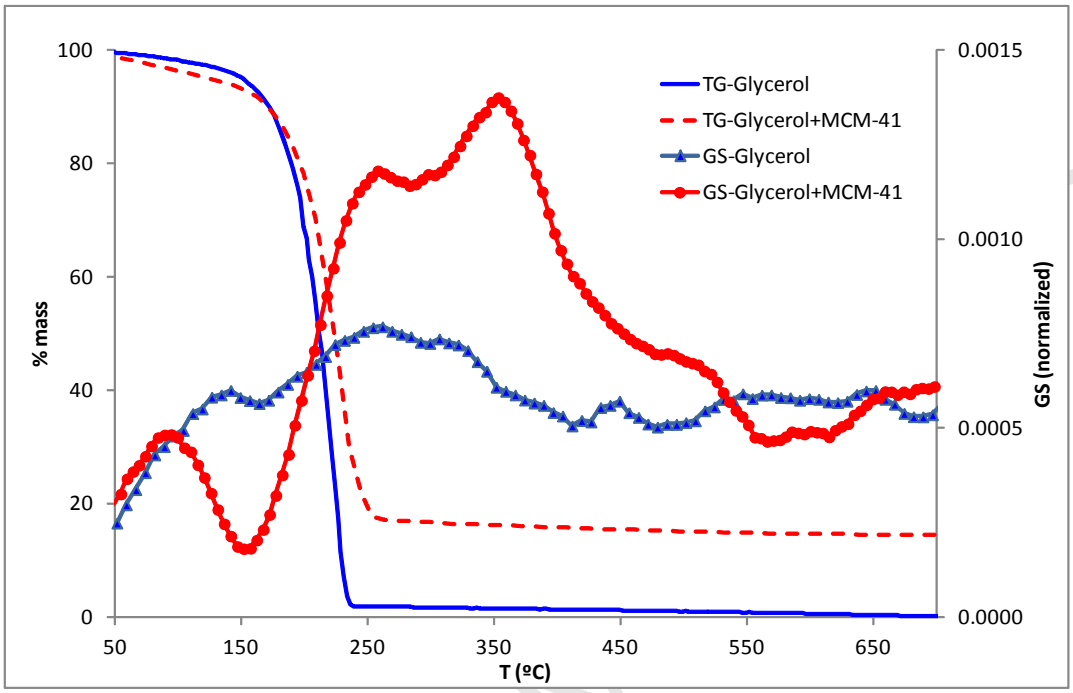

Figure 2b)

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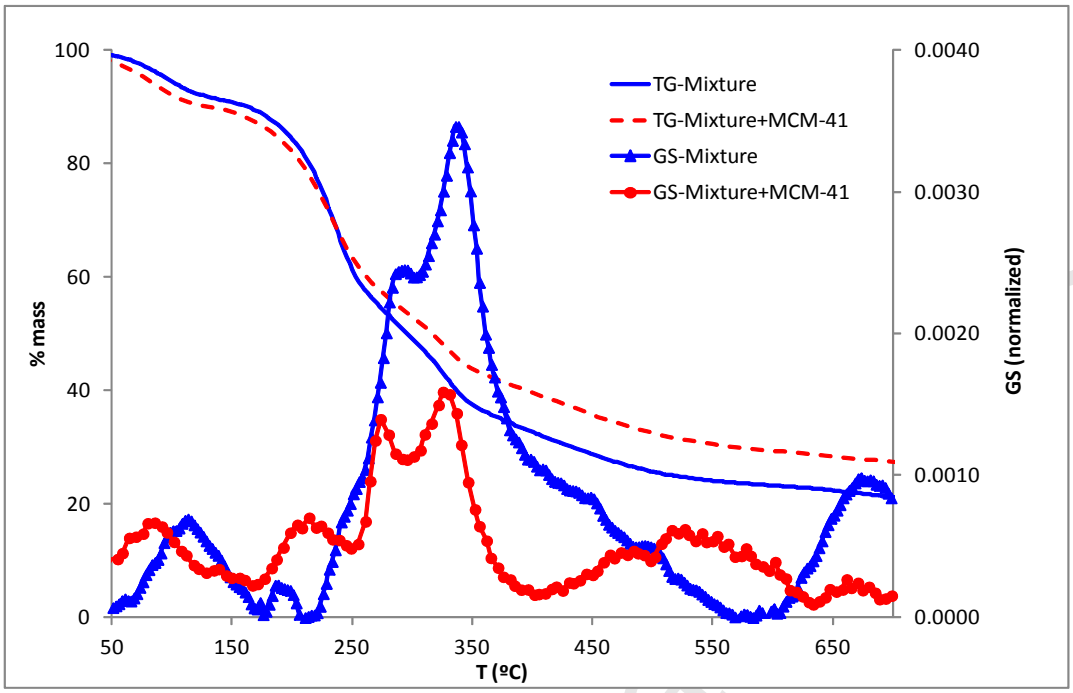

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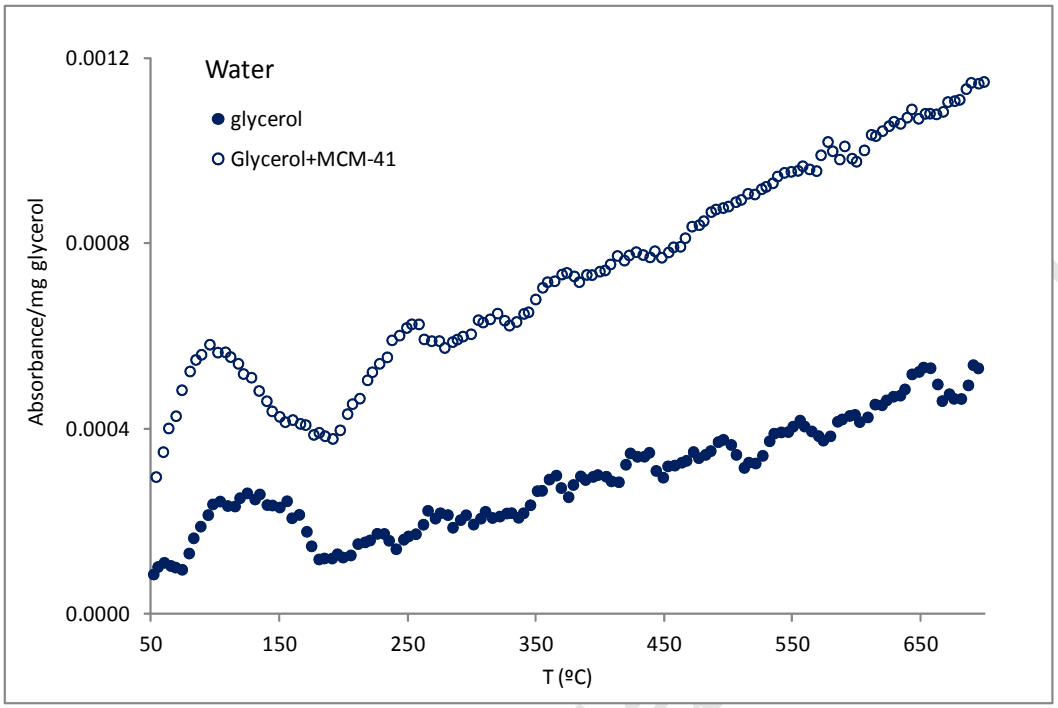
Figure 2. TGA and normalized GS curves corresponding to the pyrolysis of tobacco (a), glycerol (b) and tobacco+glycerol (c) in the absence and in the presence of MCM-41. The GS normalized curves have been obtained by dividing the GS intensity by the mass of pyrolyzable material.



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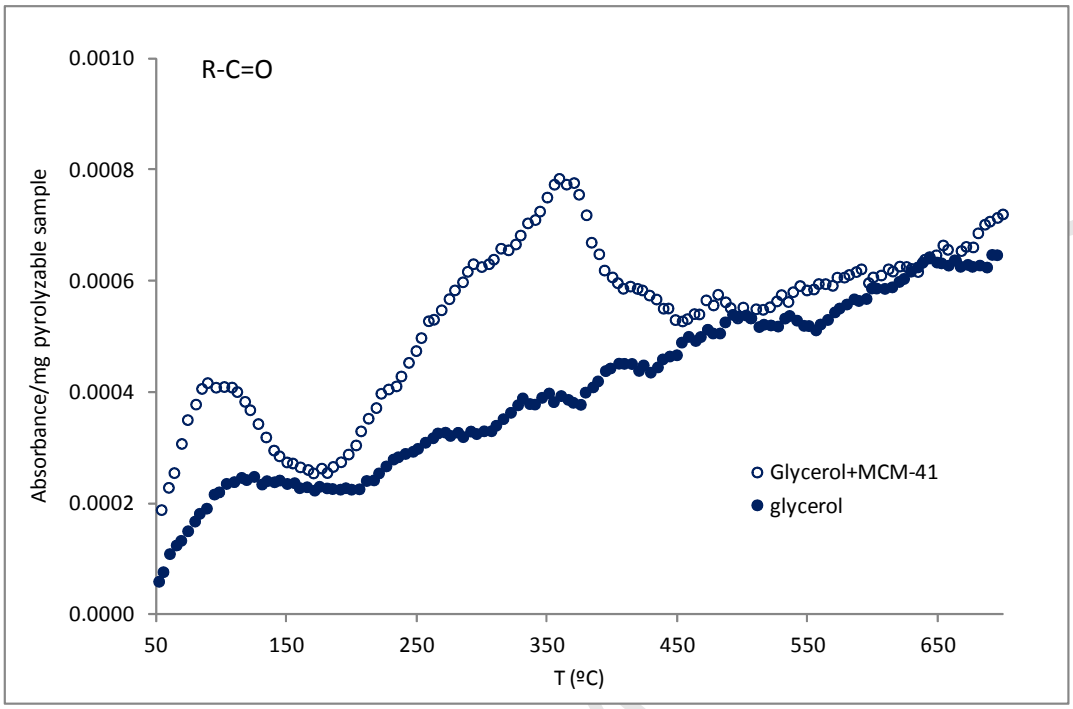

Figure 3b)

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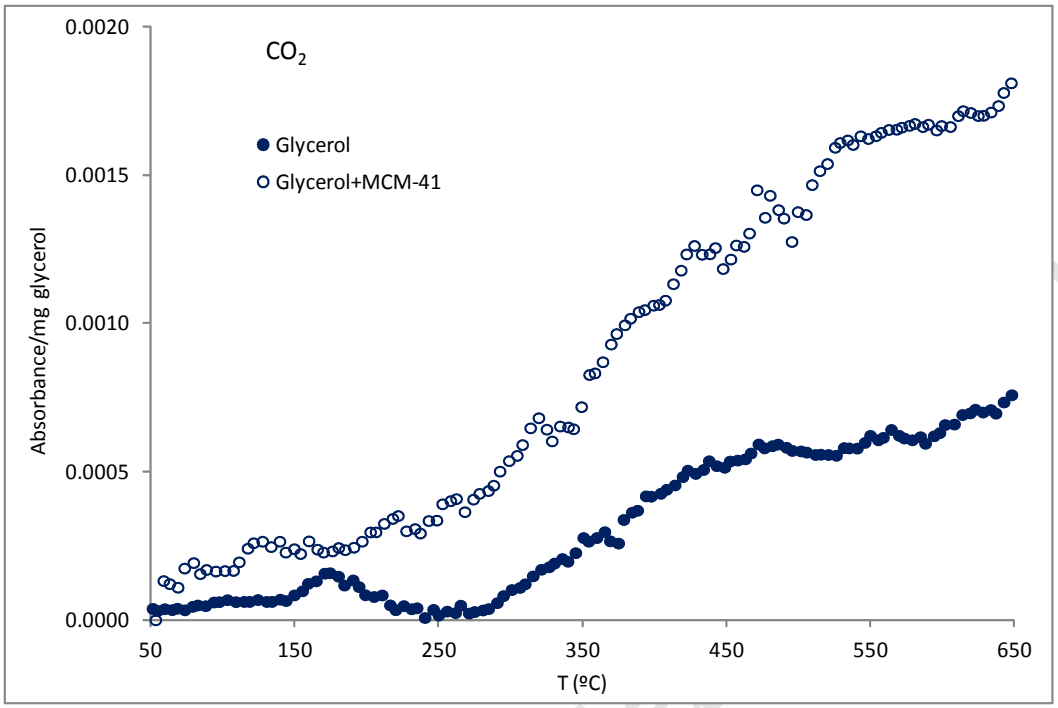

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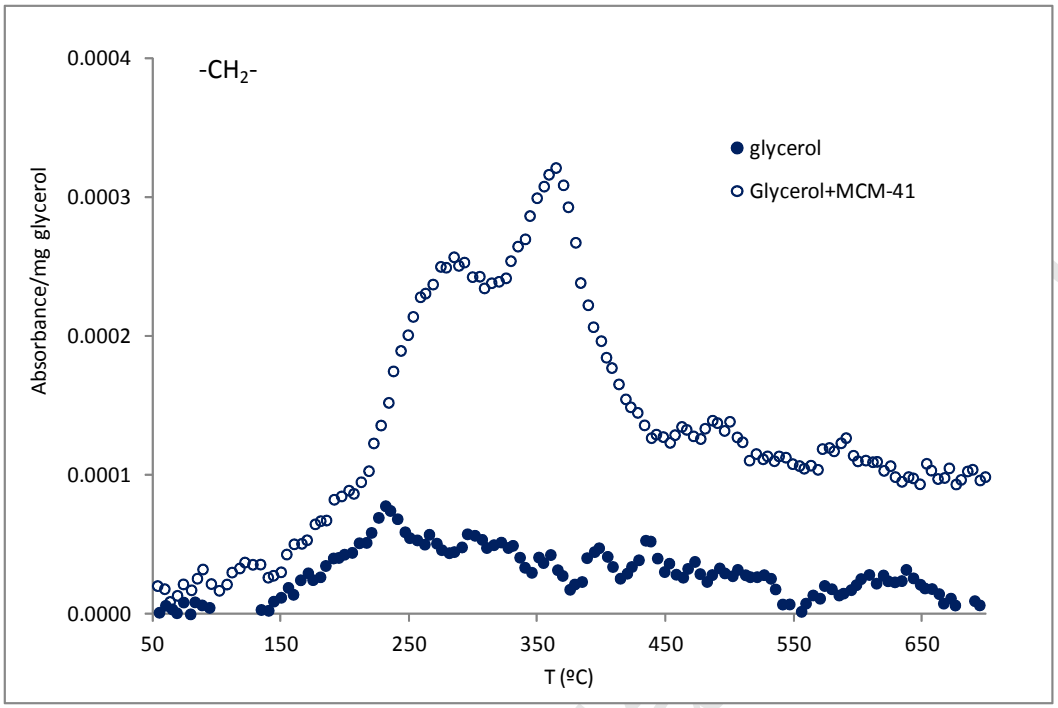

Figure 3d)

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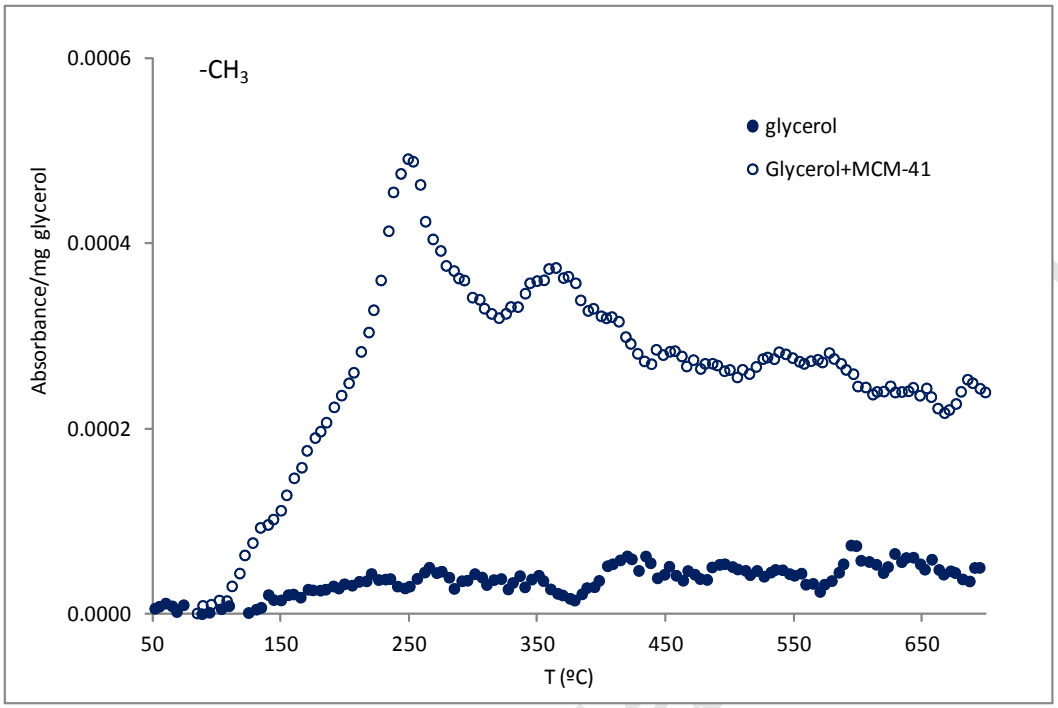
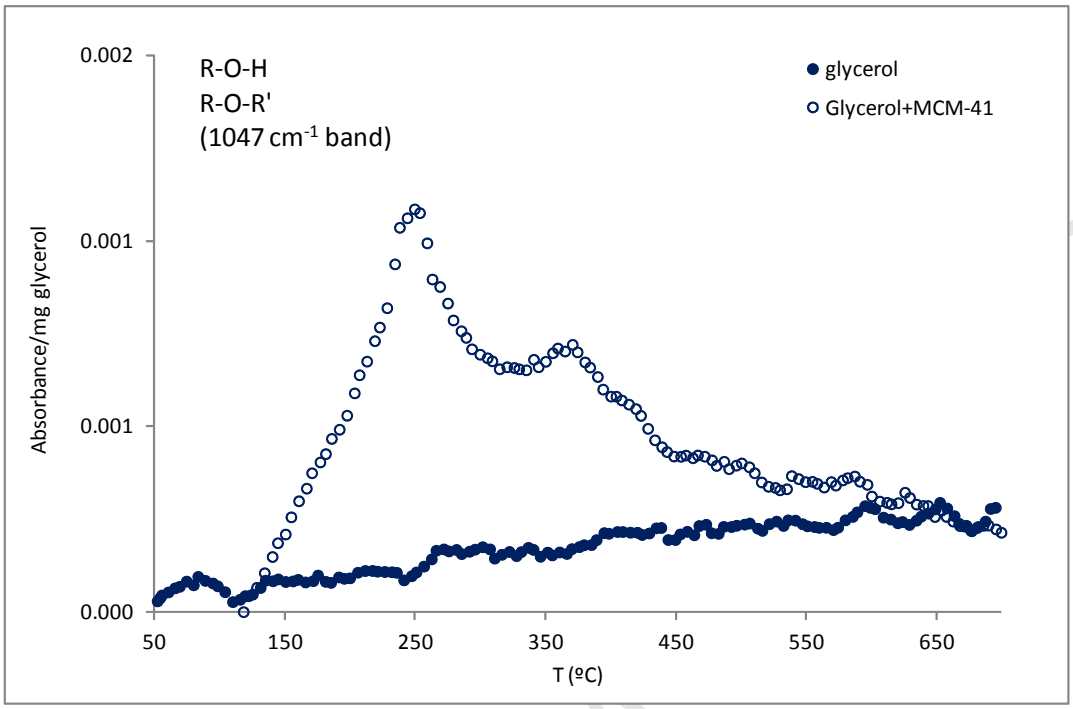


Figure 3e)

Figure 3. Evolution of different gaseous functional groups or compounds with temperature in the thermal and MCM-41 catalytic pyrolysis of tobacco and a tobacco-glycerol mixture. a) Water, b) R-C=O, c) CO_2, d) $-CH_2$, e) $-CH_3$, f) R-OH and/or R-O-R'



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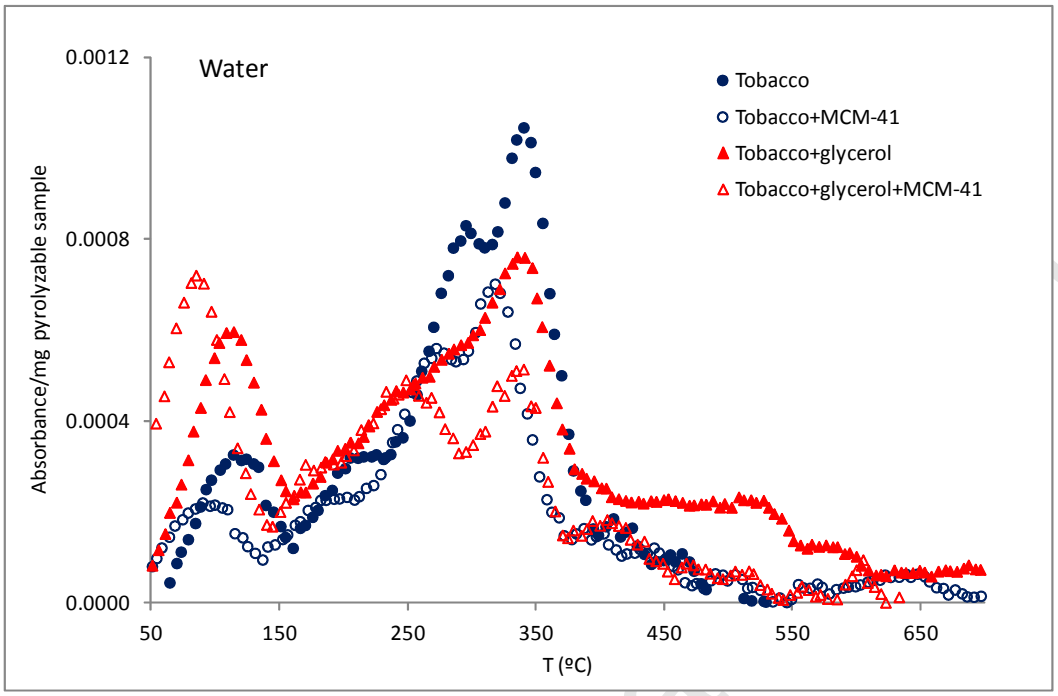

Figure 4a)

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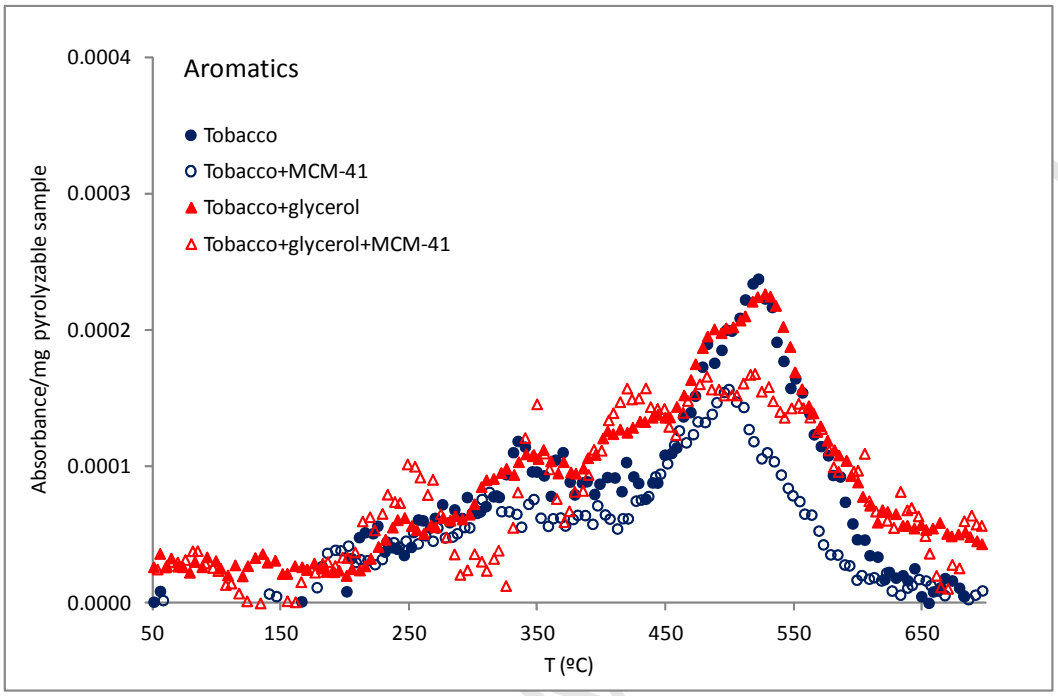

Figure 4b)

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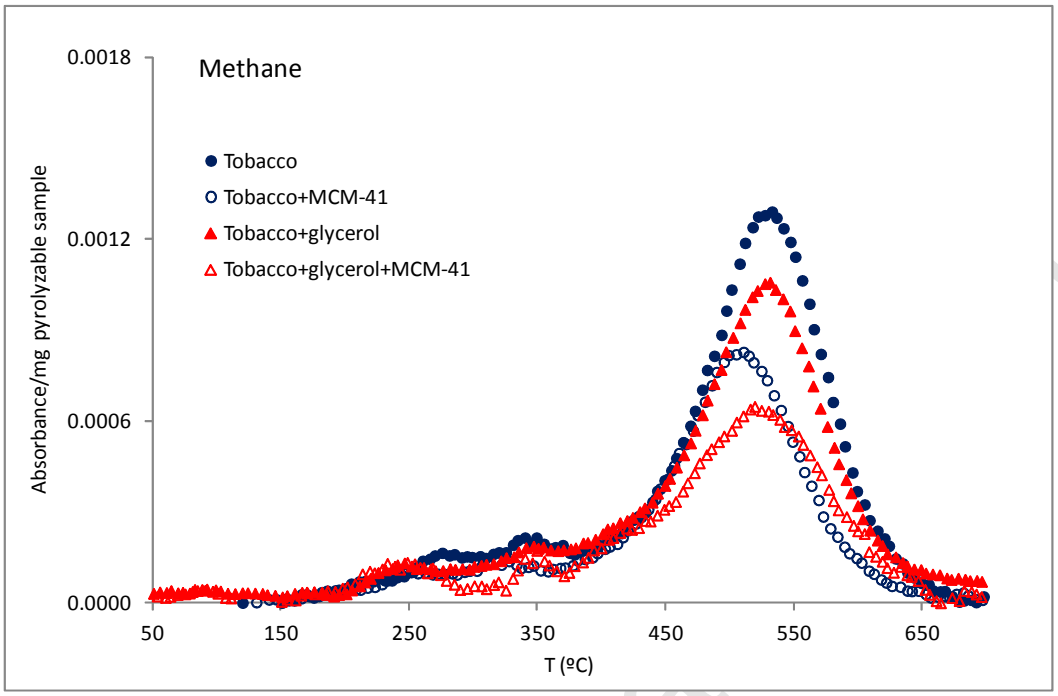

Figure 4c)

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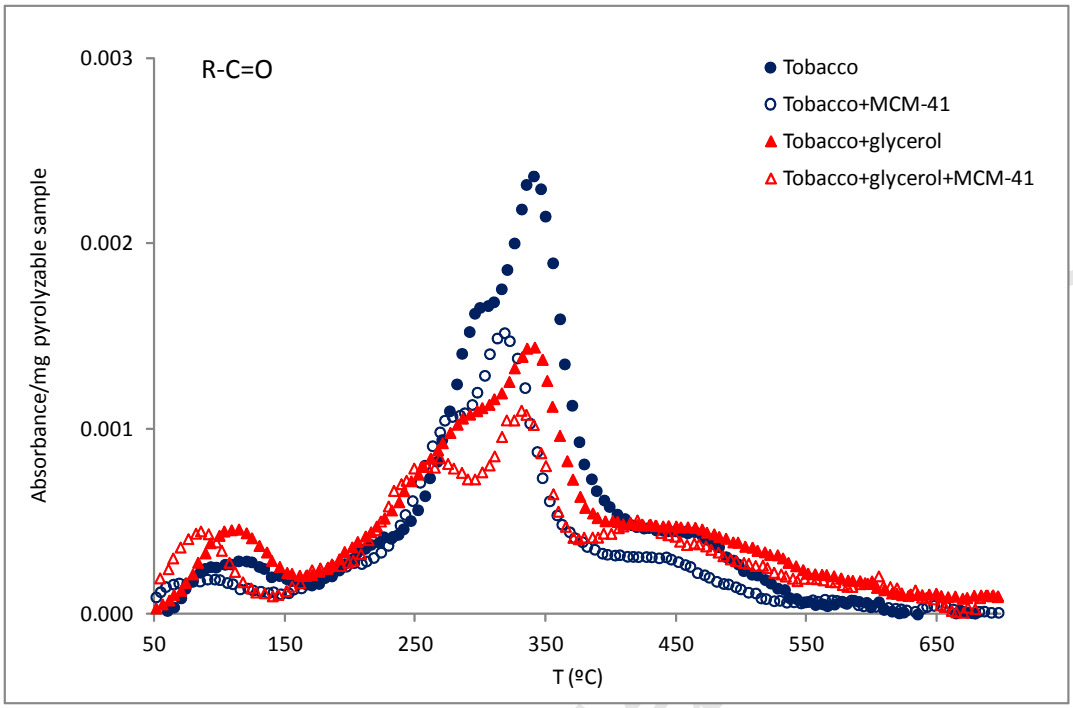

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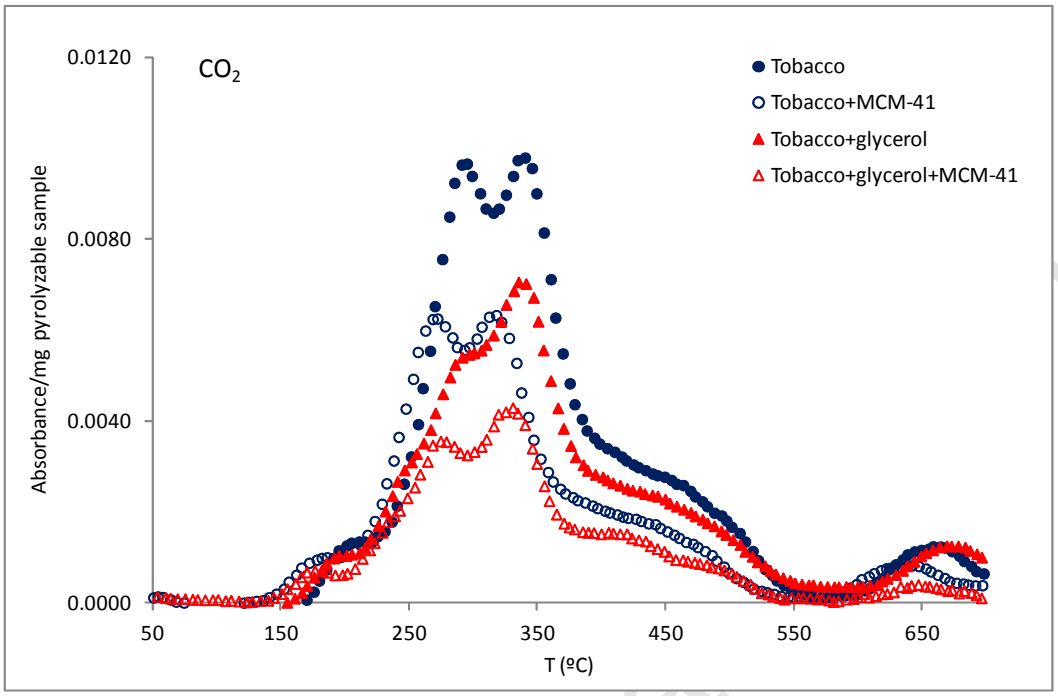

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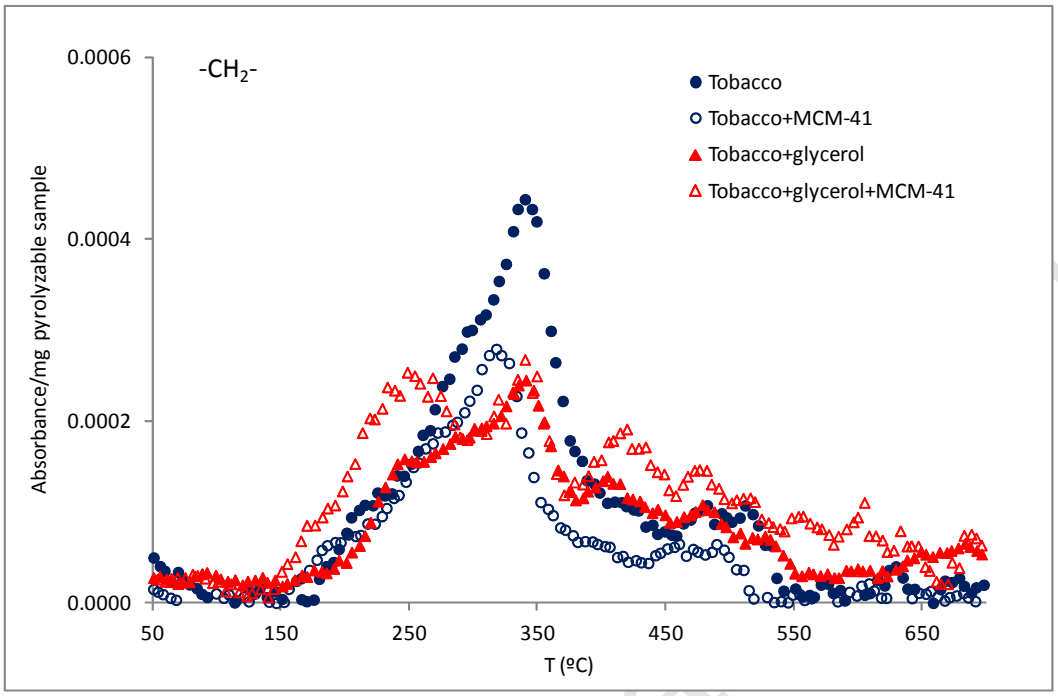

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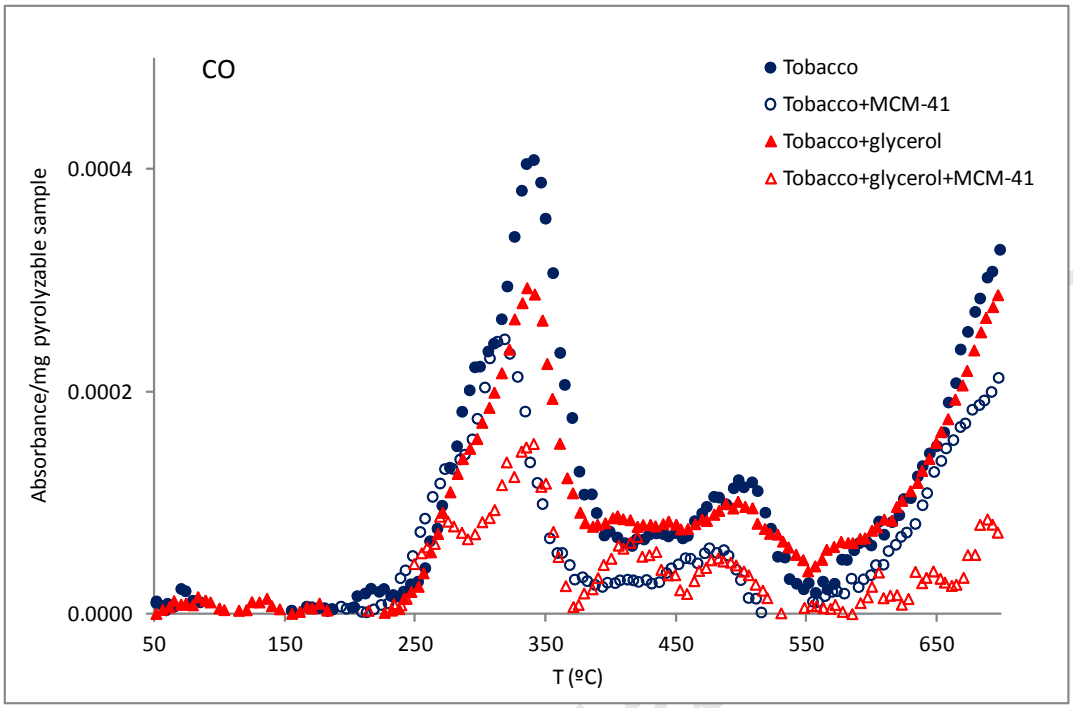

Figure 4g)

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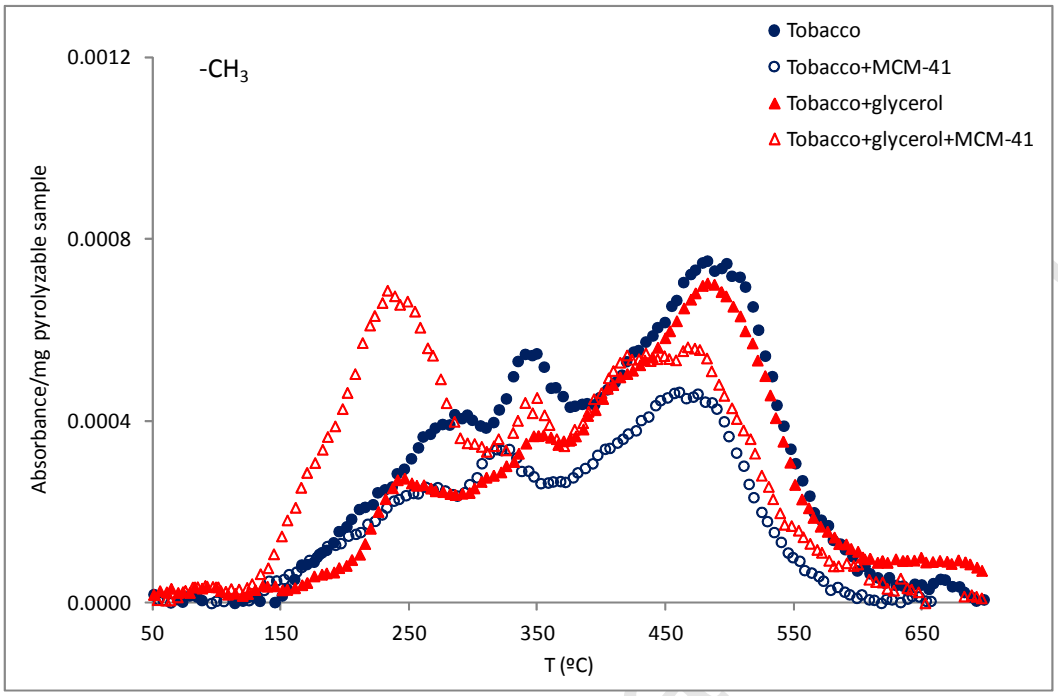

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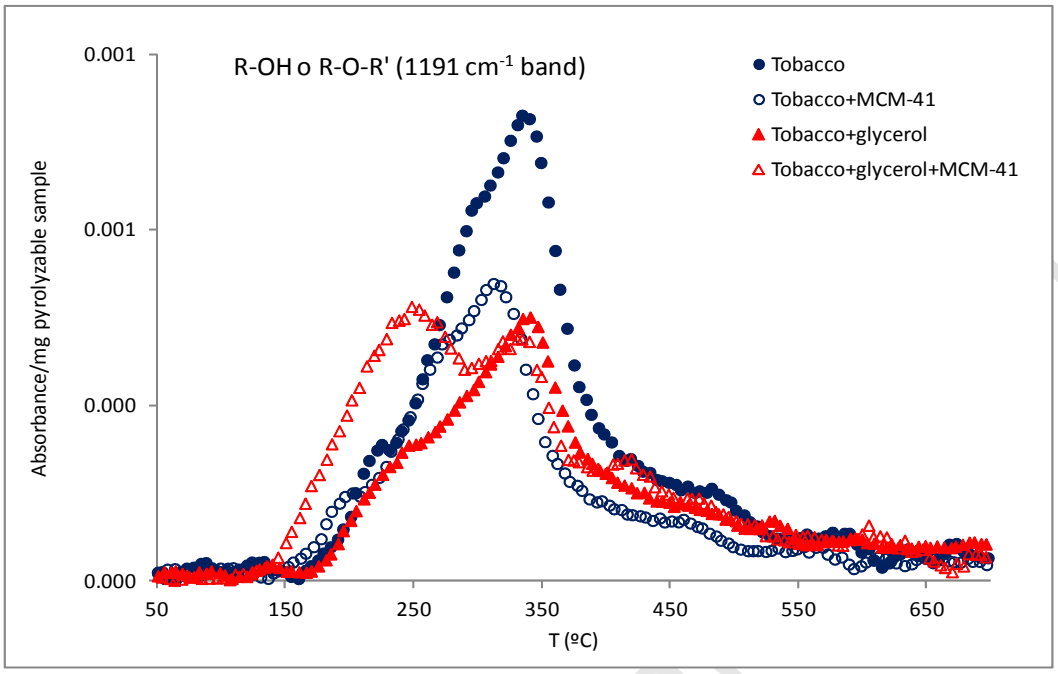

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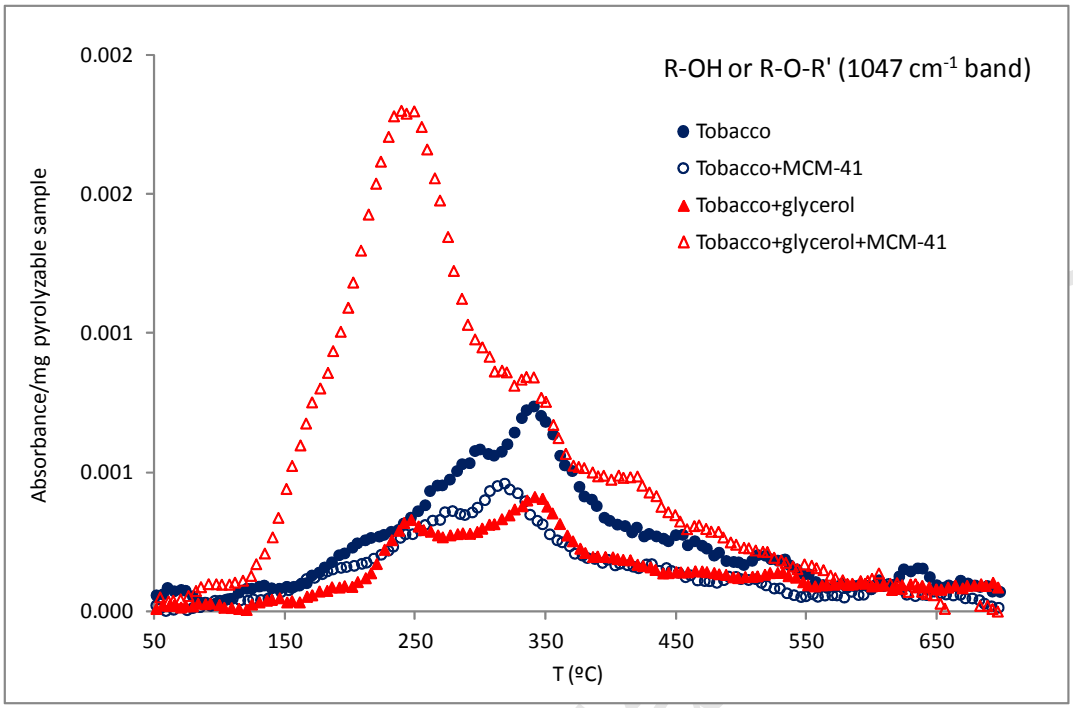

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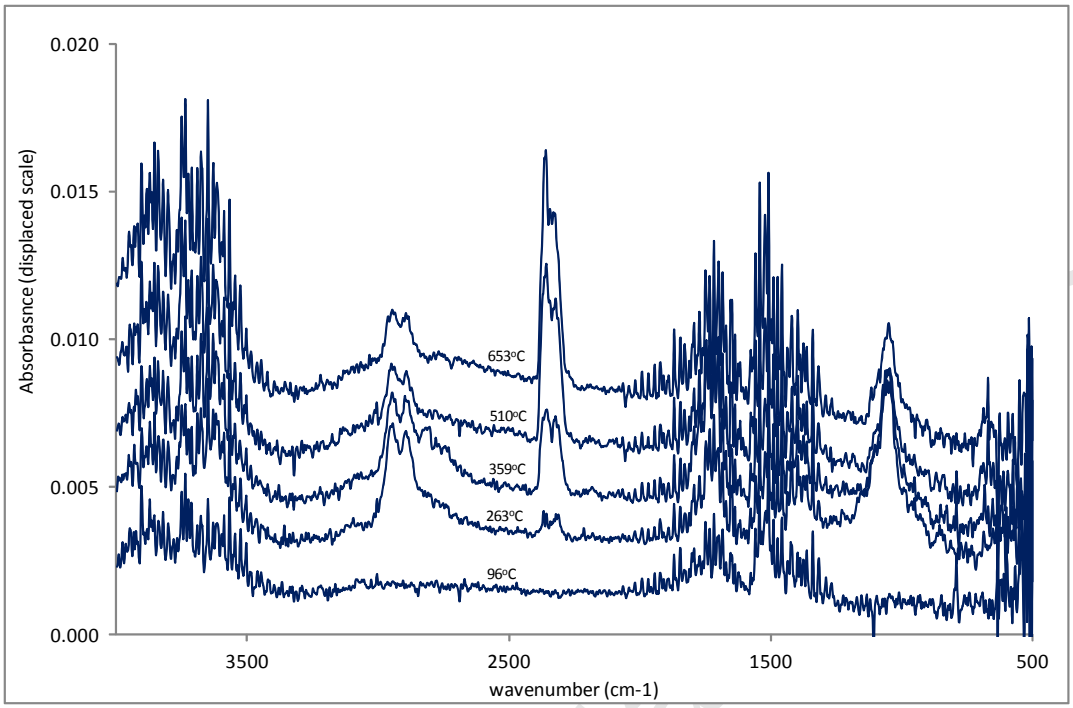

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TGA/FTIR study of the MCM-41-catalytic pyrolysis of tobacco and tobacco-glycerol mixtures

A. Gómez-Siurana*, A. Marcilla, M. Beltrán, D. Berenguer , I. Martínez-Castellanos, L. Catalá, S. Menargues

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Highlights

TGA/FTIR study of the effect of MCM-41 on the pyrolysis of glycerol, tobacco and tobacco+glycerol.

The yield of volatiles is noticeably decreased if the MCM-41 is used as a tobacco additive.

The addition of MCM-41 changes in the composition of the gases obtained at each temperature.

The catalyst decreases of the yields of methane, CO, CO_2 and carbonylic compounds.

The results obtained suggest than MCM-41 could be an additive in order to reduce tobacco toxicity.